

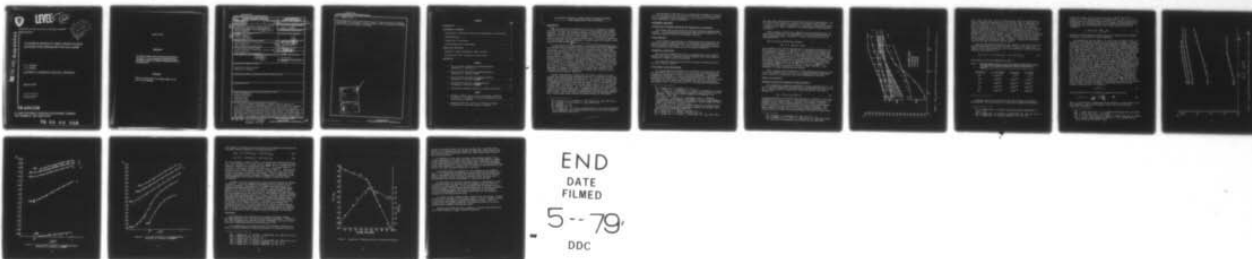
AD-A065 544

ARMY ELECTRONICS RESEARCH AND DEVELOPMENT COMMAND FO--ETC F/G 9/1  
THE POTENTIAL RECOVERY OF POROUS GRAPHITE FLUORIDE ELECTRODES A--ETC(U)  
JAN 79 H F HUNGER, J E ELLISON  
DELET-TR-79-2

UNCLASSIFIED

NL

1 OF 1  
AD  
AO 65544



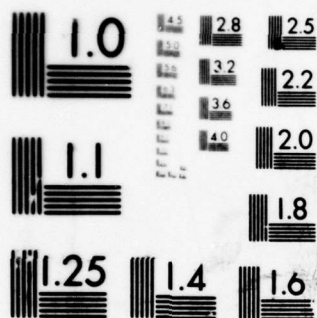
END

DATE

FILMED

5--79

DDC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A



**LEVEL II**

**(12)**

RESEARCH AND DEVELOPMENT TECHNICAL REPORT

DELET-TR-79-2



THE POTENTIAL RECOVERY OF POROUS GRAPHITE FLUORIDE  
ELECTRODES AFTER TERMINATION OF THE LOAD CURRENT

H. F. Hunger  
J. E. Ellison

ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

January 1979

DISTRIBUTION STATEMENT

Approved for public release;  
distribution unlimited.

**ERADCOM**

US ARMY ELECTRONICS RESEARCH & DEVELOPMENT COMMAND  
FORT MONMOUTH, NEW JERSEY 07703

**79 03 09 028**

DDC FILE COPY AD A0 65544

## **NOTICES**

### **Disclaimers**

The citation of trade names and names of manufacturers in this report is not to be construed as official Government indorsement or approval of commercial products or services referenced herein.

### **Disposition**

Destroy this report when it is no longer needed. Do not return it to the originator.



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER DELET-TR-79-2	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	9. Research and development
6. TITLE (and Subtitle) THE POTENTIAL RECOVERY OF POROUS GRAPHITE FLUORIDE ELECTRODES AFTER TERMINATION OF THE LOAD CURRENT.		5. TYPE OF REPORT & PERIOD COVERED Technical Report.	
7. AUTHOR(s) Herbert F./Hunger Joseph E./Ellison		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army Electronics Technology & Devices Lab ATTN: DELET-PR Fort Monmouth, New Jersey 07703		8. CONTRACT OR GRANT NUMBER(s)	
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Electronics Technology & Devices Lab ATTN: DELET-PR Fort Monmouth, New Jersey 07703		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11L 61102AH47/P9-491	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 19p.		12. REPORT DATE January 1979	
		13. NUMBER OF PAGES 14	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) State of Discharge Current Distribution Exchange Currents Transition Time Diffusion Control			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Partial or complete discharge of graphite fluoride cathodes in Li/1M LiClO <sub>4</sub> -propylene carbonate/CF <sub>0.93</sub> cells at 25°C, followed by potential rise after termination of the load current, was investigated. The quasi- steady state cathode polarization during current flow was determined using the periodically interrupted sine wave pulse current method. From these data, exchange currents of the graphite fluoride reduction and the solvent oxidation were computed as functions of load current density and theoretical cathode utilization. The changes in exchange currents were related to changes in the			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

(Cont on Reverse Side)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

410 698

LB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. ABSTRACT (Cont)

electrochemically active inner surface areas of graphite fluoride and carbon, respectively. The potential recovery follows a time relationship, indicating that the process is diffusion controlled.

ACCESSION for	
NTIS	<input checked="" type="checkbox"/> Section
DDC	<input type="checkbox"/> Section
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	SPECIAL
A	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

## CONTENTS

	<u>Page</u>
INTRODUCTION . . . . .	1
EXPERIMENTAL PROCEDURES . . . . .	2
Purification of Propylene Carbonate and Preparation of Electrolyte . .	2
Cathode Material . . . . .	2
Preparation of Electrodes . . . . .	2
Electrochemical Cell Measurements . . . . .	2
RESULTS AND DISCUSSION . . . . .	3
Mechanism to Reach Steady-State "Rest" Potential . . . . .	3
The Electrode "Rest" Potential at Steady State . . . . .	9
CONCLUSIONS . . . . .	12

## FIGURES

1. CF <sub>0.93</sub> Cathode Potentials vs Lithium Reference Electrode as a Function of $t$ . . . . .	4
2. CF <sub>0.93</sub> Cathode Potentials vs Lithium Reference Electrode as a Function of $\sqrt{t}$ . . . . .	7
3. CF <sub>0.93</sub> Cathode Potentials vs Lithium Reference Electrode as a Function of $\sqrt{t/\tau}$ . . . . .	10
4. CF Cathode Potentials vs Lithium Reference Electrode as a Function of $\sqrt{t/\tau}$ . . . . .	11
5. Logarithms of Exchange Currents vs Cathode Utilization . . . . .	13

## TABLES

1. Exchange Currents $(i_0)_{CF_n}$ (A) of the Cathodic Reduction of CF <sub>0.93</sub> as a Function of Cathode Utilization (%) and Load Current $i_c$ (mA/cm <sup>2</sup> ) . . . . .	5
2. Transition Time $\tau_j$ (sec) as a Function of Cathode Utilization (%) and Load Current $i_c$ (mA/cm <sup>2</sup> ) . . . . .	9



# THE POTENTIAL RECOVERY OF POROUS GRAPHITE FLUORIDE ELECTRODES AFTER TERMINATION OF THE LOAD CURRENT

## INTRODUCTION

The nondestructive determination of the state of discharge of primary batteries has always been of great interest to electrochemists and battery engineers. If novel electrochemical systems are introduced, with reaction mechanisms different from the classical redox reaction, the question arises whether or not such systems are more amenable to a determination of their state of discharge than the classical redox system. This was the case with the lithium/organic electrolyte/graphite fluoride system which showed a mixed potential at the cathode.<sup>1,2</sup>

It was observed that there exists a relationship between the open circuit potential and the cathode utilization in  $\text{Li}/\text{CF}_n$  cells after termination of the load. In cells where the amount of cathode material limits their ampere-hour capacity, the "rest" cathode potentials or "rest" cell voltages can be directly related to the state of discharge of the cathode and of the cell or battery. Tiedemann observed that potentiostatically measured polarization data of fluorographite electrodes were a function of their state of discharge (up to 10 percent).<sup>3</sup> He also confirmed our finding that the open circuit potential of a porous fluorographite electrode is a mixed potential and a function of its state of discharge. He further found that the voltage recovery of a porous fluorographite electrode after termination of the load was a function of its discharge state and he related the voltage recovery phenomenon to changes in the charge of the double layer capacity of the electrode and presented an equation for estimating the relaxation time as a function of the state of discharge.<sup>4</sup>

Further investigations revealed that the cathode potential (or cell voltage) rise could be used to determine the state of discharge of lithium/organic electrolyte/graphite fluoride cells.<sup>5</sup> For a given cell design, size, and geometry, and an optimum rise time of 5 to 10 minutes, the average error of determining the state of discharge was within 7.8 to 9.3 percent for the complete range of discharge and a current density range of 0.2 - 2.0  $\text{mA}/\text{cm}^2$  of geometrical cross section. Far less favorable results were obtained in relating cathode polarization data or exchange currents to the state of discharge of the cathode, especially in intermittent operation or if a change of load occurred. Any method used to determine the state of discharge requires that a quasi-steady state condition be reached during the load period.

<sup>1</sup>H. F. Hunger and G. J. Heymach, J. Electrochem. Soc. 120, 1161 (1973).

<sup>2</sup>N. Tiedemann, J. Electrochem. Soc. 121, 1308 (1974).

<sup>3</sup>N. Tiedemann, op. cit.

<sup>4</sup>N. Tiedemann, op. cit.

<sup>5</sup>H. F. Hunger and J. E. Ellison, "Determination of the State of Discharge of Lithium/Organic Electrolyte/Graphite Fluoride Cells," R&D Technical Report ECOM-4391, March 1976.

The objective of this report is to describe the mechanism of the potential rise of graphite fluoride cathodes in 1M LiClO<sub>4</sub> in propylene carbonate at room temperature after termination of a load current and to relate the "rest" potentials to kinetic parameters.

## EXPERIMENTAL PROCEDURES

### Purification of Propylene Carbonate and Preparation of Electrolyte

The solvent used in this study was propylene carbonate (Eastman Kodak Company). Its purification procedures have been described previously.<sup>6</sup> The electrolyte used was 1M LiClO<sub>4</sub> in propylene carbonate.

### Cathode Material

A grey graphite fluoride (CF<sub>0.93</sub>), obtained from Rice University, was used as the active cathode material. Its preparation and characteristics have been reported previously.<sup>7</sup> The nickel fluoride impurities introduced in the preparation were removed by use of a powder classifier.<sup>8</sup>

### Preparation of Electrodes

The dry press technique<sup>9</sup> was used in the preparation of the cathodes, whereby a dry mixture of graphite fluoride, graphite, and Teflon powder is pressed into a highly porous nickel matrix.

Both anode and reference electrode were prepared by pressing lithium foil onto a nickel screen.<sup>10</sup>

### Electrochemical Cell Measurements

The electrochemical measurements were performed in an open Teflon cell. All experimental work was performed in a dry lab (Dri-Lab/Dri-Train/Vacuum Atmospheres Corporation) in a pure, dried argon atmosphere. Fluorographite cathodes were discharged at various current densities and polarization measurements were made versus a lithium reference electrode. The periodically interrupted sine wave pulse current technique was used for polarization measurements free of the ohmic iR drop.<sup>11,12</sup> All polarization measurements

---

<sup>6</sup>H. F. Hunger and G. J. Heymach, op. cit., p. 1.

<sup>7</sup>A. J. Valerga, R. B. Budachhape, G. D. Parks, P. Kamarchick, J. L. Wood, and J. L. Margrave, "Thermodynamic and Kinetic Data of Carbon Fluorine Compounds," Final Report, Contract DAAB07-73-C-0056 (ECOM), Rice University, March 1974.

<sup>8</sup>J. L. Wood, A. J. Valerga, R. B. Budachhape, and J. L. Margrave, "Thermodynamic, Electrochemical and Synthetic Studies of the Graphite-Fluorine Compounds CF and C<sub>4</sub>F," Final Report, Contract DAAB07-72-C-0105 (ECOM), Rice University, December 1972.

<sup>9</sup>H. F. Hunger and J. E. Ellison, "Cathodic Reduction of Carbon-Fluorine and Carbon-Nitrogen-Fluorine Compounds in Organic Electrolytes," R&D Technical Report ECOM-4296, March 1975.

<sup>10</sup>H. F. Hunger and G. J. Heymach, op. cit., p. 1.

<sup>11</sup>H. F. Hunger and J. E. Ellison, ECOM-4296, op. cit.

<sup>12</sup>H. F. Hunger and J. E. Ellison, J. Electrochem. Soc. 122, 1288 (1975).

were made under quasi-steady state conditions; they were characterized, e.g., for a load current density of  $1 \text{ mA/cm}^2$ , by a potential decay of about  $-1 \text{ mV/min}$  for the range of discharge up to 10 percent of theoretical cathode utilization and of about  $-6 \text{ mV/min}$  for the range between 75 and 90 percent utilization.

Before exchange currents were computed from the polarization data, one quantitative criterion for the applicability of the Tafel approximation in porous electrodes, namely, uniformity of current distribution, had to be fulfilled.<sup>13,14,15</sup>

With the current distribution parameter

$$\delta = L \cdot I \cdot \beta (1/K + 1/\sigma) \quad (1)$$

the uniformity of the current distribution in the porous electrode over the Tafel region was checked. In Equation (1),  $L$  represents the thickness of a one-dimensional, porous electrode in cm,  $I$  the overall current density,  $\beta$  is equal to  $(1 - \alpha)nF/RT$ ,  $K$  is the conductivity of the pore electrolyte in mho/cm, and  $\sigma$  the conductivity of the electrode matrix in mho/cm. If  $\delta \leq 0.1$ , the current distribution is uniform. In conducting these experiments,  $L$  was approximately  $10^{-2} \text{ cm}$  (thickness of compressed cathode mix),  $I = 10^{-3} \text{ A/cm}^2$  (the maximum current density in the linear region of the potential-current relationship),  $\beta \approx 20$ ,  $K = 4.9 \cdot 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ , and  $\sigma = 6.9 \Omega^{-1} \text{ cm}^{-1}$ . Inserting these data in Equation (1) yields for  $\delta = 4.08 \cdot 10^{-2}$ . Thus, uniformity of current distribution was assured.

After a desired state of discharge of the cathodes was reached, the load current was interrupted and the rise of the cathode potential was measured with a recorder as a function of time after termination of the load.

## RESULTS AND DISCUSSION

### Mechanism to Reach the Steady-State "Rest" Potential

From intermittent discharge experiments at current densities of 0.2, 0.5, and  $1.0 \text{ mA/cm}^2$  of geometrical electrode area, with interruptions after 10, 25, 50, 75, and 100 percent of theoretical cathode utilization, according to Equation (2),



the mixed potentials at the cathode were measured as a function of time after termination of the load current. In Figure 1 these cathode potentials ( $V_c$ ) measured versus a lithium reference electrode in  $1\text{M LiClO}_4$  in propylene carbonate at about  $25^\circ\text{C}$  are plotted versus the log of rise time in seconds, and as a function of load current density and cathode utilization. The figure shows in principle that, due to higher cathode polarization, the cathode potential is lower for previously higher loads than for lower loads

<sup>13</sup>N. Tiedemann, J. Electrochem. Soc. 121, op. cit., p. 1.

<sup>14</sup>J. S. Newman and C. W. Tobias, J. Electrochem. Soc. 109, 1183 (1962).

<sup>15</sup>J. Euler and W. Nonnenmacher, Electrochim. Acta 2, 268 (1960).



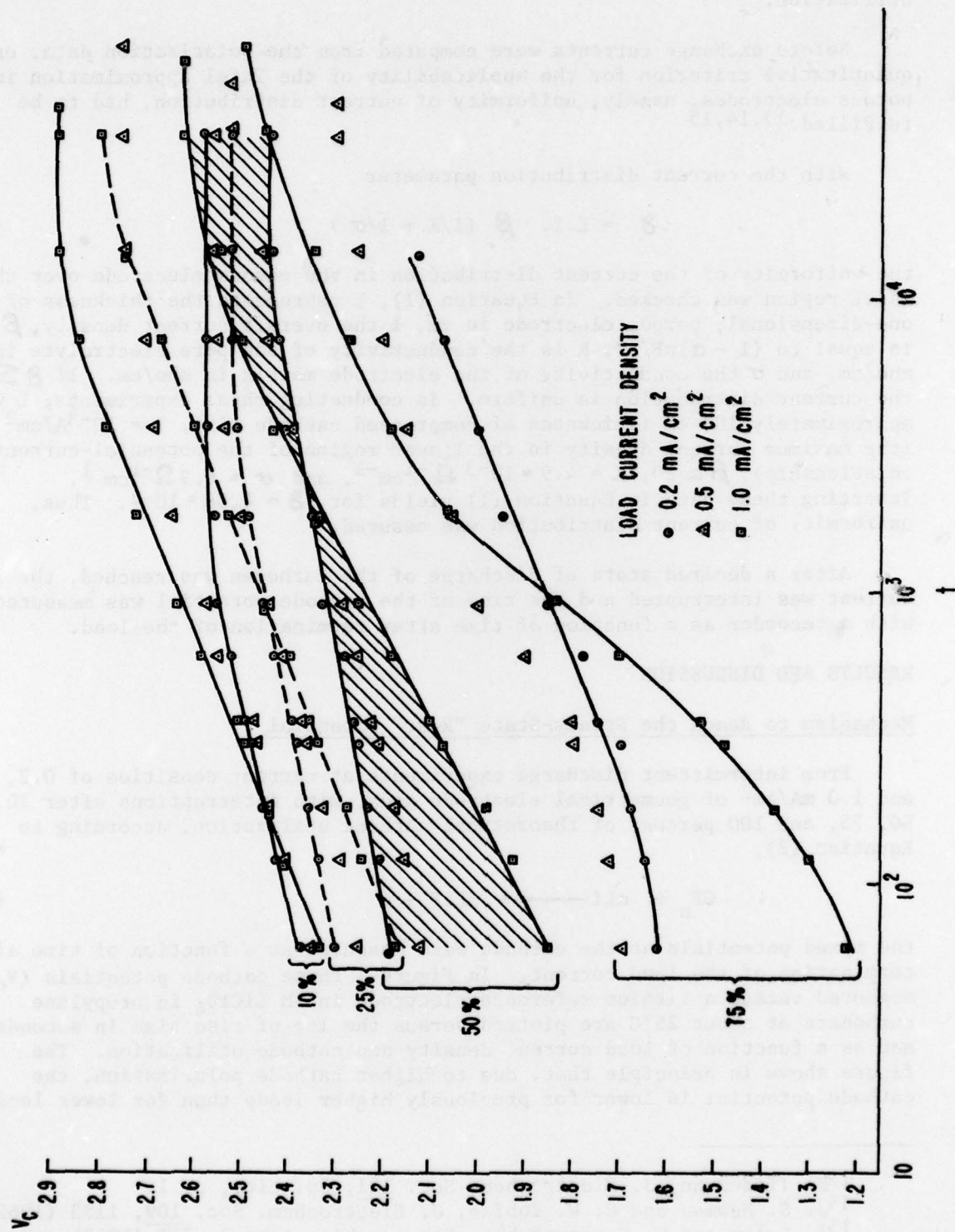


Figure 1.  $CF_{0.93}$  Cathode Potentials vs Lithium Reference Electrode as a Function of  $t$ .

after a short rise time. After a crossover point, which is significant for state of discharge determination if a load current range is considered, the reverse becomes true. The electrode with the lower, initial load shows a lower rest potential after a sufficiently long rise time. The crossover point is significant in that it indicates the optimum rise time for a defined cathode utilization where a minimum error in determining the state of discharge from  $V_c$  can be expected, e.g., for a cathode utilization of 10%, the optimum rise time is about 3 minutes, for 25%, 15 minutes, for 50%, 42 minutes, for 75%, 17 minutes, and for 100%, 9 minutes. The average over the whole range of cathode utilization is about 17 minutes. Using a different method for determining the optimum rise time, a value of 15 minutes was previously found for the same load current density range.<sup>16</sup>

From the cathode polarization data,  $\eta_c$ , measured at the end of the intermittent discharge periods, exchange currents,  $(i_o)_{CF_n}$ , were computed as a function of the load currents,  $i_c$ , and of the theoretical cathode utilization, using the Tafel Equation (3).<sup>17</sup>

$$\eta_c = 4.57 - V_c = 0.116 \log i_c - 0.116 \log (i_o)_{CF_n} \quad (3)$$

The exchange currents are summarized in Table 1.

Table 1. Exchange Currents  $(i_o)_{CF_n}$  (A) of the Cathodic Reduction of  $CF_{0.93}$  as a Function of Cathode Utilization (%) and Load Current  $i_c$  (mA/cm<sup>2</sup>)

Utilization	$i_c = 0.2 \text{ mA/cm}^2$	$0.5 \text{ mA/cm}^2$	$1.0 \text{ mA/cm}^2$
10%	$2.8 \cdot 10^{-23}$	$10^{-23}$	$10^{-23}$
25%	$1.4 \cdot 10^{-23}$	$4.5 \cdot 10^{-24}$	$4.7 \cdot 10^{-25}$
50%	$1.8 \cdot 10^{-24}$	$5.6 \cdot 10^{-25}$	$1.9 \cdot 10^{-27}$
75%	$2.0 \cdot 10^{-29}$	$3.2 \cdot 10^{-28}$	$2.2 \cdot 10^{-33}$
100%	$2.0 \cdot 10^{-38}$	$6.3 \cdot 10^{-36}$	$6.3 \cdot 10^{-41}$

Exchange currents for utilizations less than 10% have been reported previously.<sup>18</sup> For a load current of  $1.0 \text{ mA/cm}^2$  and cathode utilizations of

<sup>16</sup>H. F. Hunger and J. E. Ellison, R&D Technical Report ECOM-4391, op. cit., p. 1.

<sup>17</sup>H. F. Hunger and J. E. Ellison, J. Electrochem. Soc. 122, op. cit., p.2.

<sup>18</sup>H. F. Hunger and J. E. Ellison, ECOM-4391, op. cit., p. 1.

0.065 and 2 percent, the exchange currents are  $5.4 \cdot 10^{-21}$  and  $10^{-22}$  A, respectively. The exchange current is a measure for the rate of the anodic-cathodic current at the equilibrium potential,  $E_{CF_n}$ , and its sensitivity to disturbances. The exchange currents of the graphite fluoride reduction are a measure for the electrochemically active, inner surface areas of the cathodes.<sup>19</sup>

$$i_o = \text{prop.} S \cdot \exp(-\Delta G_{\text{act}}/RT) \quad (4)$$

Therefore, various changes in surface area can be expected with increasing utilization for various load current densities.

By comparing the data in Table 1, it can be seen, in general, that if  $i_c$  is smaller, the remaining graphite fluoride area will be larger. At higher cathodic current densities, the surface area apparently decreases faster with increasing utilization than at lower current densities. This finding seems to be valid up to 50 percent utilization, e.g., after 10 percent utilization, the cathode discharged at  $0.2 \text{ mA/cm}^2$  still has the highest  $i_o$  or largest  $CF_n$  area. This is also reflected in the high, initial position of the potential rise curve (Figure 1), since an electrode with a larger inner surface area will have a lesser polarization at the starting point of the voltage rise than an electrode with a smaller surface area. At higher current densities, a more rapid disappearance of the  $CF_n$  surface area is probably connected with the rapid formation of carbon surface, in accordance with Equation (2), in a surface rich modification. Thus, a higher current density apparently creates a carbon structure at the cathode which facilitates the faster attainment of the rest potentials after termination of the load. The question concerning the mechanism of the potential rise after termination of the load was answered diagnostically with plots of the cathode potential versus the log of the square root of the rise time as a function of cathode utilization (%) (Figure 2). Prior load current density was  $0.2 \text{ mA/cm}^2$ . The plots show an initially linear rise followed by reaching a flat plateau. This behavior indicates that a concentration change of a species codetermining the mixed electrode potential occurs at the cathode surface with  $\sqrt{t}$ , at first very rapid and later on slower and slower. The pertinent equations can be derived, using a similar procedure like Weber,<sup>20</sup> Sand,<sup>21</sup> and Vetter,<sup>22</sup> but the boundary conditions had to be changed to

$$c_j(X,0) = c_o \quad (5)$$

This was obtained for the concentration change at the electrode

$$c_j(0,t) = c_o + \frac{2}{\sqrt{\pi}} \cdot \frac{i_m}{n F} \frac{v_j}{D_j} \cdot \sqrt{t} \quad (6)$$

where  $c_o$  is the initial concentration at the interface,  $i_m$  the current at the mixed potential,  $v_j$  the stoichiometric factor, and  $D_j$  the diffusion coefficient of species  $j$ .

<sup>19</sup>G. J. Young, "Fuel Cells," p. 42, Reinhold Publishing Corp., N.Y. (1960).

<sup>20</sup>H. F. Weber, Wied. Ann. 7, 536 (1879).

<sup>21</sup>H. J. S. Sand, Phil. Mag. 1, 45 (1900); Z. Physik. Chem. 35, 641 (1900).

<sup>22</sup>K. J. Vetter, "Elektrochemische Kinetik," p. 182, Springer Verlag, Berlin-Göttingen-Heidelberg (1961).



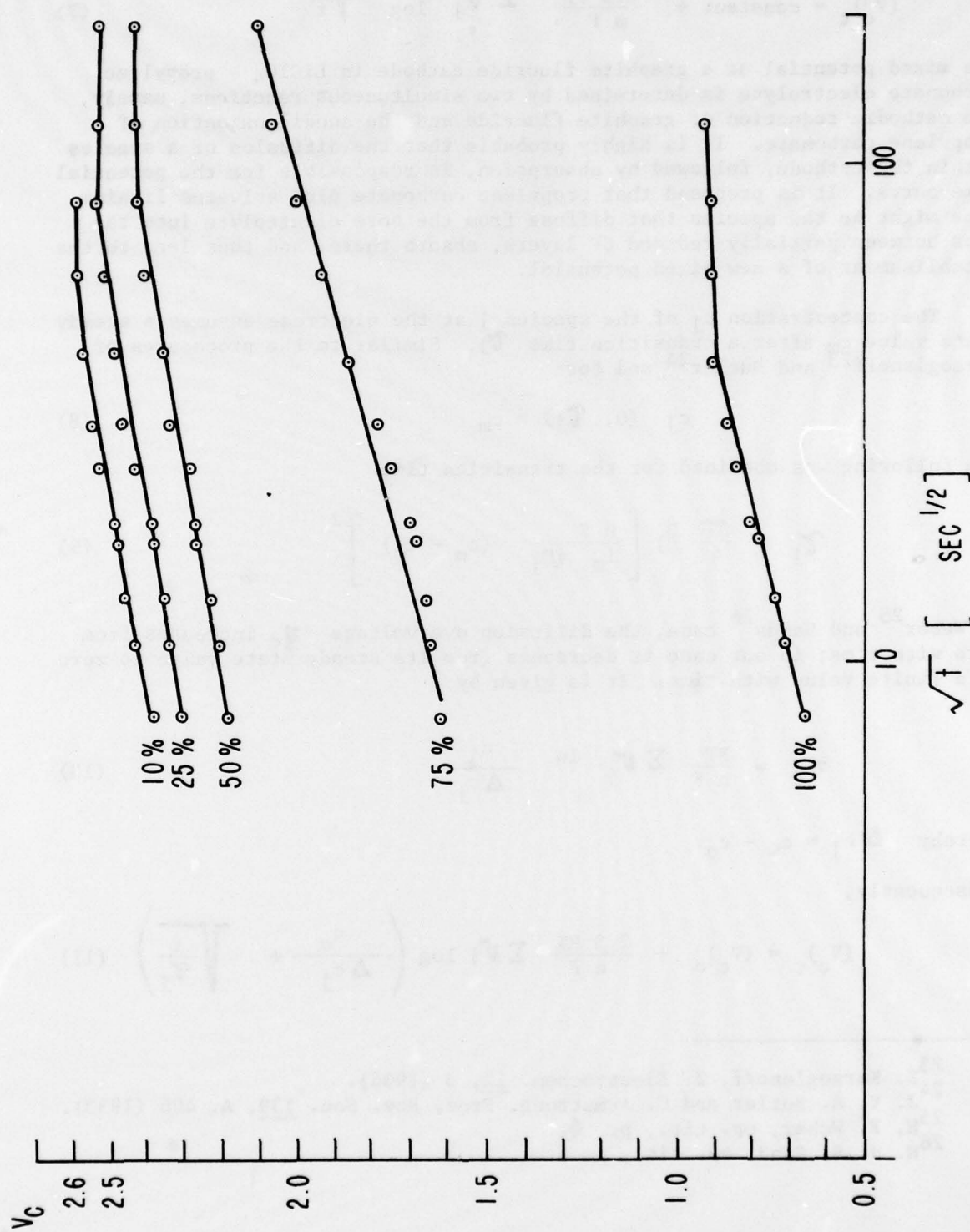


Figure 2.  $CF_{0.93}$  Cathode Potentials vs Lithium Reference Electrode as a Function of  $\sqrt{t}$

From Equation (6) and the Nernst Equation, the cathode potential-time relationship can be derived:

$$(V_c)_t = \text{constant} + \frac{2.3 RT}{n F} \sum \nu_j \log \sqrt{t} \quad (7)$$

The mixed potential at a graphite fluoride cathode in  $\text{LiClO}_4$  - propylene carbonate electrolyte is determined by two simultaneous reactions, namely, the cathodic reduction of graphite fluoride and the anodic oxidation of propylene carbonate. It is highly probable that the diffusion of a species within the cathode, followed by absorption, is responsible for the potential time curve. It is proposed that propylene carbonate plus solvated lithium ions might be the species that diffuse from the pore electrolyte into the gaps between partially reduced CF layers, absorb there, and thus lead to the establishment of a new mixed potential.

The concentration  $c_j$  of the species  $j$  at the electrode assumes a steady state value  $c_m$  after a transition time  $\tau_j$ . Similar to the procedures of Karaoglanoff<sup>23</sup> and Butler<sup>24</sup> and for:

$$c_j(0, \tau_j) = c_m \quad (8)$$

the following was obtained for the transition time

$$\tau_j = \frac{JT}{4} D_j \left[ \frac{n F}{i_m \nu_j} (c_m - c_o) \right]^2 \quad (9)$$

In Weber<sup>25</sup> and Sands<sup>26</sup> case, the diffusion overvoltage  $\eta_d$  increases from zero with time; in our case it decreases from its steady state value to zero or a finite value with time. It is given by

$$\eta_d = \frac{RT}{n F} \sum \nu_j \ln \frac{c_j}{\Delta c_j} \quad (10)$$

whereby  $\Delta c_j = c_m - c_o$ .

Consequently,

$$(V_c)_t = (V_c)_o + \frac{2.3 RT}{n F} \sum \nu_j \log \left( \frac{c_o}{\Delta c_j} + \sqrt{\frac{t}{\tau_j}} \right) \quad (11)$$

<sup>23</sup>Z. Karaoglanoff, Z. Electrochem. 12, 5 (1906).

<sup>24</sup>J. V. A. Butler and G. Armstrong, Proc. Roy. Soc. 139, A. 406 (1933).

<sup>25</sup>H. F. Weber, op. cit., p. 6.

<sup>26</sup>H. J. S. Sand, op. cit., p. 6.

For a strong initial cathodic polarization  $c_o \rightarrow 0$ ; therefore, if the process is diffusion controlled, a plot of the cathode potential versus

$\log \sqrt{\frac{t}{\tau_j}}$  should be linear.

Since the transition time,  $\tau_j$ , is a function of both the cathode utilization and the load current density prior to interruption, this has to be considered in preparing the plots. Table 2 shows experimental transition times; they are the times required to reach a constant rest potential after load current interruption. These transition times vary with  $i_c$  and cathode utilization since they are influenced by the diffusion rate which will be different in the various structures formed.

Table 2. Transition Time  $\tau_j$  (sec) as a Function of Cathode Utilization (%) and Load Current  $i_c$  (mA/cm<sup>2</sup>)

$i_c$	UTILIZATION				
	10%	25%	50%	75%	100%
0.2	3,600	7,200	14,400	21,600	28,800
1.0	18,000	28,800	46,800	64,800	82,800

Using these experimental  $\tau_j$  values, the  $V_c$  versus  $\log \sqrt{t/\tau}$  plots were computed and are shown in Figures 3 and 4 as a function of cathode utilization (%). In Figure 3 the prior load current density was 0.2 mA/cm<sup>2</sup> and the plot shows linear behavior up to  $\sqrt{t/\tau} = 1$ ; in Figure 4 the prior load current density was 1.0 mA/cm<sup>2</sup> and the same behavior up to 50 percent utilization with increasing deviations from linearity at higher utilizations was observed.

#### The Electrode "Rest" Potential at Steady State

After the transition time,  $\tau_j$ , steady state potentials are reached at the cathodes.

Using the mixed potential theory, the value of the steady state rest potential and its dependence upon the state of discharge can be explained. Two effects are causing a lowering of the cathode potential with increasing cathode utilization: the disappearance of graphite fluoride surface area and the appearance of new carbon surface area in accordance with Equation (12).



In case of a single organic solvent, the cell voltage  $E_m$ , a mixed potential, which is numerically identical to the cathode potential measured versus a lithium reference electrode, can be expressed by

$$E_m = \frac{E_{CF}^\circ}{2} + \frac{E_s^\circ}{2} + 0.058 \log \frac{(i_o)_{CF}}{(i_o)_s} \quad (13)$$



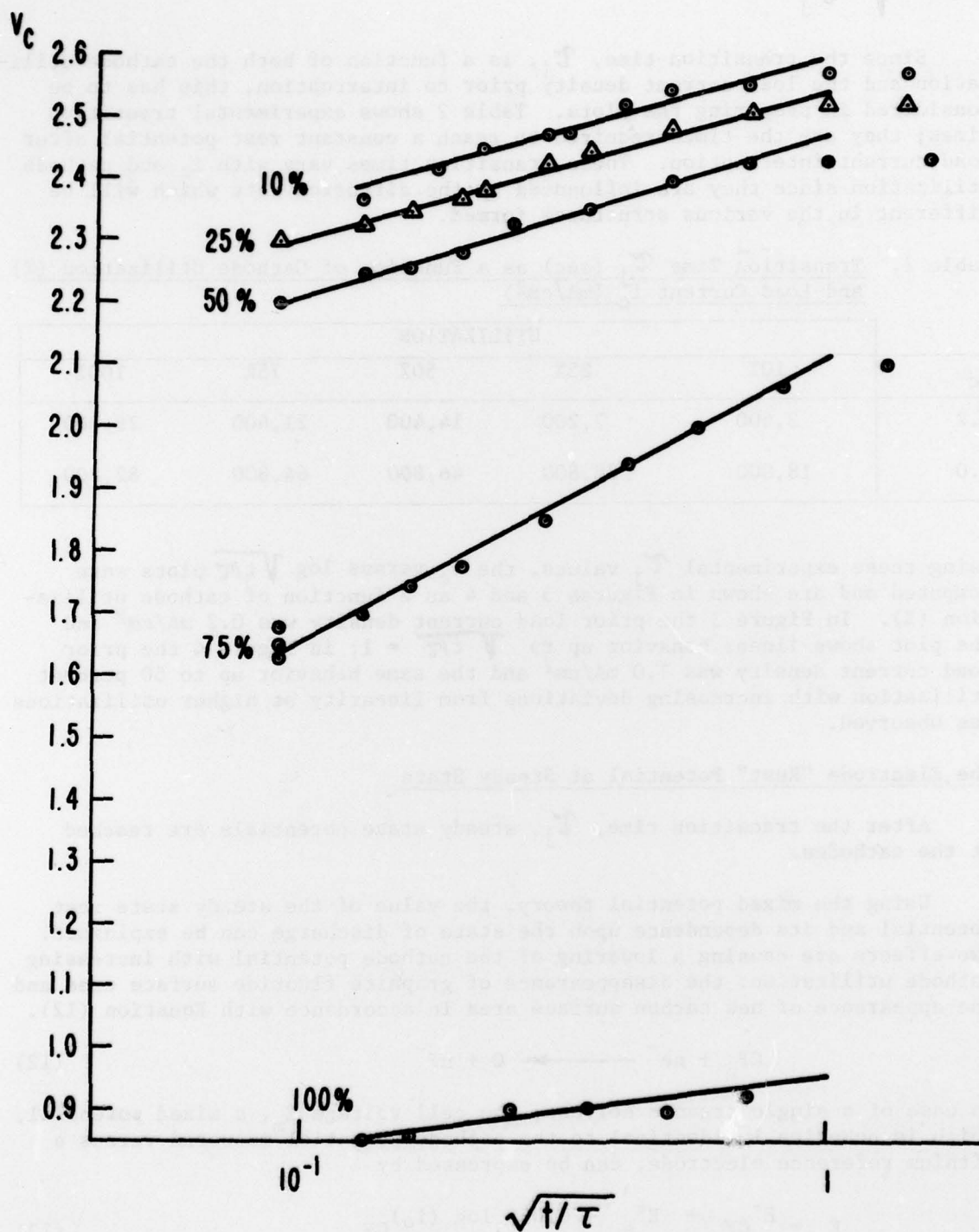


Figure 3.  $CF_{0.93}$  Cathode Potentials vs Lithium Reference Electrode as a Function of  $\sqrt{t/\tau}$

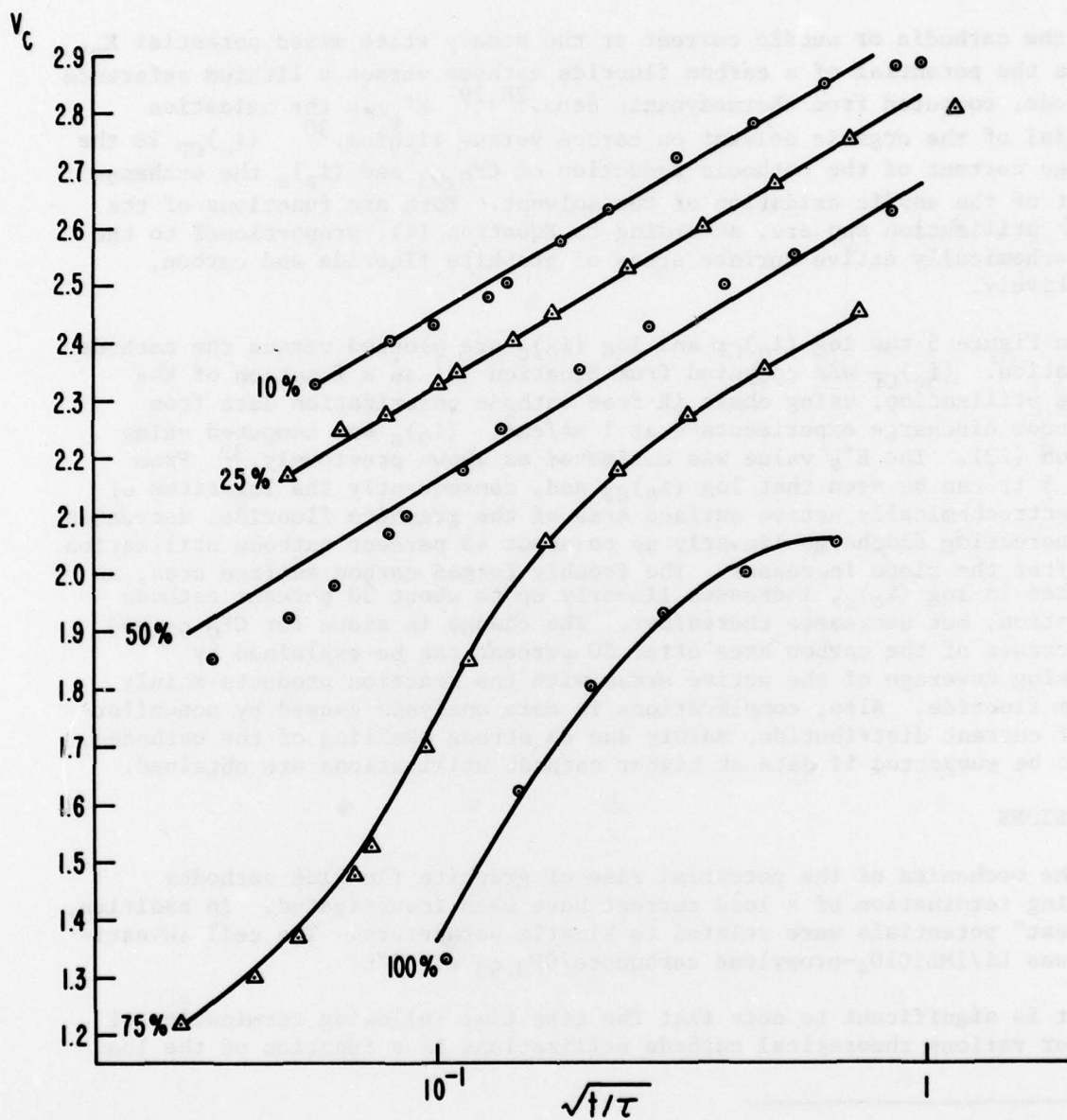


Figure 4. CF Cathode Potentials vs Lithium Reference Electrode as a Function of  $\sqrt{t/\tau}$

This equation is derived from the equations for the cathodic CF reduction and the anodic solvent oxidation at the mixed potential.<sup>27</sup>

$$E_{CF}^{\circ} - E_m = 0.116 \log i_m - 0.116 \log (i_o)_{CF} \quad (14)$$

$$E_m - E_s^{\circ} = 0.116 \log i_m - 0.116 \log (i_o)_s \quad (15)$$

$i_m$  is the cathodic or anodic current at the steady state mixed potential  $E_m$ .  $E_{CF}^{\circ}$  is the potential of a carbon fluoride cathode versus a lithium reference electrode, computed from thermodynamic data.<sup>28,29</sup>  $E_s^{\circ}$  is the oxidation potential of the organic solvent on carbon versus lithium.<sup>30</sup>  $(i_o)_{CF}$  is the exchange current of the cathodic reduction of  $CF_{0.93}$  and  $(i_o)_s$  the exchange current of the anodic oxidation of the solvent. Both are functions of the cathode utilization and are, according to Equation (4), proportional to the electrochemically active surface areas of graphite fluoride and carbon, respectively.

In Figure 5 the  $\log (i_o)_{CF}$  and  $\log (i_o)_s$  are plotted versus the cathode utilization.  $(i_o)_{CF}$  was computed from Equation (3) as a function of the cathode utilization, using ohmic iR free cathode polarization data from continuous discharge experiments<sup>31</sup> at 1 mA/cm<sup>2</sup>.  $(i_o)_s$  was computed using Equation (13). The  $E_s^{\circ}$  value was estimated as shown previously.<sup>32</sup> From Figure 5 it can be seen that  $\log (i_o)_{CF}$  and, consequently the logarithm of the electrochemically active surface area of the graphite fluoride, decreases with increasing discharge linearly up to about 45 percent cathode utilization. Thereafter the slope increases. The freshly formed carbon surface area, as reflected in  $\log (i_o)_s$ , increases linearly up to about 50 percent cathode utilization, but decreases thereafter. The change in slope for  $CF_{0.93}$  and the decrease of the carbon area after 50 percent can be explained by increasing coverage of the active areas with the reaction products mainly lithium fluoride. Also, complications in data analysis caused by nonuniformity of current distribution, mainly due to strong swelling of the cathodes, have to be suspected if data at higher cathode utilizations are obtained.

## CONCLUSIONS

The mechanism of the potential rise of graphite fluoride cathodes following termination of a load current have been investigated. In addition, the "rest" potentials were related to kinetic parameters. The cell investigated was Li/1MLiClO<sub>4</sub>-propylene carbonate/ $CF_{0.93}$  at 25°C.

It is significant to note that the rise time following termination of load for various theoretical cathode utilizations is a function of the load

<sup>27</sup>H. F. Hunger and J. E. Ellison, J. Electrochem. Soc. 122, op.cit.,p.2.

<sup>28</sup>A. J. Valerga, et al., op. cit., p. 2.

<sup>29</sup>J. L. Wood, et al., op. cit., p. 2.

<sup>30</sup>H. F. Hunger and J. E. Ellison, J. Electrochem. Soc. 122, op.cit.,p.2.

<sup>31</sup>H. F. Hunger and J. E. Ellison, ECOM-4391, op. cit., p. 1.

<sup>32</sup>H. F. Hunger and J. E. Ellison, ECOM-4296, op. cit., p. 2.



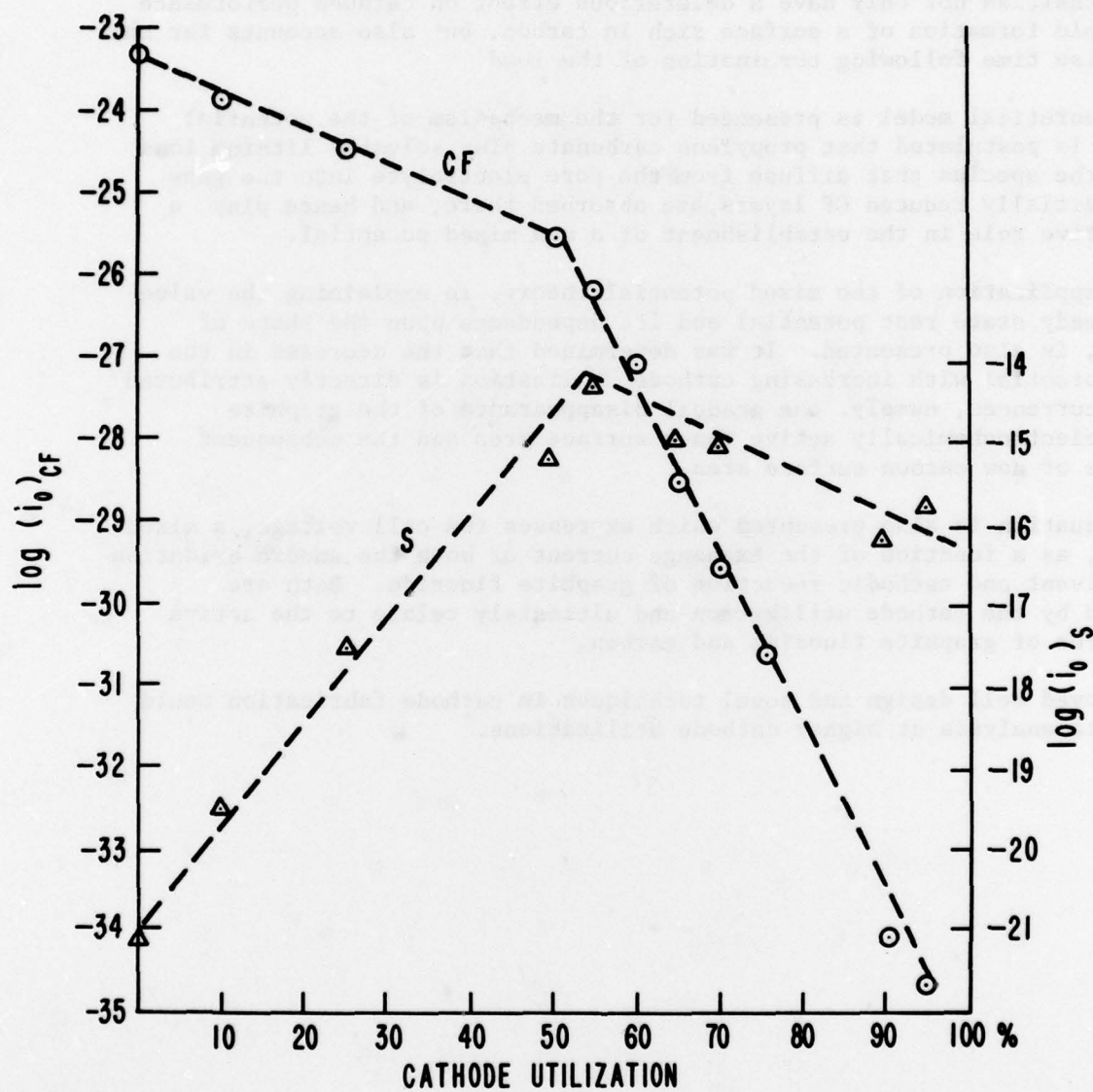


Figure 5. Logarithms of Exchange Currents vs Cathode Utilization

current, and further analysis of the data reveals that a crossover point exists for the optimum rise time between the higher and lower current loads. The crossover point being highly significant, particularly when related to practical applications.

An examination of the data collected on the exchange current of the cathodic reduction of the  $\text{CF}_{0.93}$  electrodes and its relationship to changes in the electrochemically active inner surface areas, shows that the higher current densities not only have a deleterious effect on cathode performance by the rapid formation of a surface rich in carbon, but also accounts for the shorter rise time following termination of the load.

A theoretical model is presented for the mechanism of the potential rise. It is postulated that propylene carbonate plus solvated lithium ions might be the species that diffuse from the pore electrolyte into the gaps between partially reduced CF layers, are absorbed there, and hence play a determinative role in the establishment of a new mixed potential.

The application of the mixed potential theory, in explaining the value of the steady state rest potential and its dependence upon the state of discharge, is also presented. It was determined that the decrease in the cathode potential with increasing cathode utilization is directly attributed to two occurrences, namely, the gradual disappearance of the graphite fluoride electrochemically active inner surface area and the subsequent appearance of new carbon surface area.

An equation is also presented which expresses the cell voltage, a mixed potential, as a function of the exchange current of both the anodic oxidation of the solvent and cathodic reduction of graphite fluoride. Both are influenced by the cathode utilization and ultimately relate to the active surface area of graphite fluoride and carbon.

Improved cell design and novel techniques in cathode fabrication would aid in data analysis at higher cathode utilizations.